

# $1/f$ noise in chemical reactions

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## Abstract

A chemical system consisting of two species, one of which evolves deterministically and independently of the other, which in turn is driven by the dynamics of the former and by an additional multiplicative Gaussian white noise, displays a  $1/f$  noise for intermediate to large frequencies. A novel mechanism responsible for the  $1/f$  noise is suggested.

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Although systems exhibiting  $1/f^\alpha$  noise, and related systems which display power-law type distributions, are abundant in nature, there is no generally accepted explanation for their origin and ubiquity. Self-organized criticality [1] has been proposed as such an explanation, but it has been pointed out that the notion of self-organized criticality and  $1/f^\alpha$  are mutually exclusive in many cases [2]. Recently the emergence of power-law distributions and long-time temporal correlations have been explained for example in terms of a generalized logistic systems [3]. More importantly, Davidsen and Schuster in Ref. [4] have proposed a mechanism explaining the origin of  $1/f^\alpha$ ,  $\alpha \simeq 1$ , noise in the low-frequency regime, which corresponds to very long lasting temporal correlations. The systems considered in Ref. [4] were driven by a Gaussian white noise (GWN) — in other words, no preexisting power-law distributions or fractal noises have been assumed, even implicitly. Power-law distributions have also been shown to result, at the level of the mathematical formalism used, from non-linear transformation between various stochastic variables for a very wide class of underlying “fundamental” distributions [5].

In the present Letter we consider a simple chemical system consisting of two species. Dynamics of one of the species, A, is subjected to a multiplicative GWN and is further affected by the dynamics of the other species, B. The dynamics of B is purely deterministic and is not influenced back by the dynamics of A. Such a system can be realized experimentally. We show that our model system exhibits  $1/f$  noise for intermediate to large frequencies.

Consider two chemical species, A and B. Let B decay autocatalytically and catalyse a decay of A:



The downarrows mean that species  $A^*$ ,  $B^*$  are stable and do not enter any reactions of interest. If the amounts of reagents are periodically incremented from outside

$$j_a(t) = a_0 \sum_n \delta(t - nT), \quad j_b(t) = b_0 \sum_n \delta(t - nT), \quad (3)$$

the kinetics of reactions (1)–(2) can be expressed as

$$\dot{a} = -Kab + j_a(t), \quad \dot{b} = -k_b b^2 + j_b(t), \quad (4)$$

where  $a, b$  are concentrations of A and B, respectively. We further assume that the rate at which A decays fluctuates around a deterministic value

$$K = k_a + \kappa\eta(t), \quad (5)$$

where  $\eta(t)$  is a GWN with  $\langle\eta(t)\rangle = 0$ ,  $\langle\eta(t)\eta(t')\rangle = \sigma^2\delta(t-t')$ , and all higher correlations factorize. Reactions (1)–(2) with the above constraints can be realized experimentally in a flow reactor, for instance by a photoactivated chemical reaction with a radiation field acting as a source of noise [6]; see also [7] and references quoted therein.

Because of the  $\delta$ -terms in the fluxes, we solve (4) in a stroboscopic representation. Between the pulses

$$b(t) = \frac{b_n}{1 + k_b b_n(t - nT)}, \quad nT < t < (n+1)T, \quad (6)$$

where  $b_n = b(t = nT^+)$ . The pulses simply increment the concentrations by  $a_0$  and  $b_0$ , respectively. Thus

$$b_{n+1} = b_0 + \frac{b_n}{1 + b_n k_b T}, \quad (7a)$$

$$a(t) = \frac{a_n}{(1 + b_n k_b(t - nT))^\mu} \exp\left(-\int_{nT^+}^t \kappa\eta(t')b(t')dt'\right), \quad (7b)$$

$$nT < t < (n+1)T,$$

$$a_{n+1} = a_0 + \frac{a_n}{(1 + b_n k_b T)^\mu} E_n, \quad (7c)$$

where  $a_n = a(t = nT^+)$ ,  $\mu = k_a/k_b$  is a ratio of deterministic reaction rates and

$$E_n = \exp\left(-\int_{nT^+}^{(n+1)T^-} \kappa\eta(t')b(t')dt'\right). \quad (8)$$

The  $\{b_n\}$  form a deterministic series convergent to

$$b_\infty = \frac{b_0}{2} \left( 1 + \sqrt{1 + \frac{4}{b_0 k_b T}} \right). \quad (9)$$

Note that  $b_\infty > b_0$ . Contrariwise, the series  $\{a_n\}$  is stochastic and its realizations need not to be convergent; only the series of expectation values  $\{\langle a_n \rangle\}$  can. Both  $a_n$  and  $E_n$  are random numbers, but since  $a_n$  depends only on times prior to  $nT$ ,  $a_n$  and  $E_n$  are defined on disjoint intervals and for  $\eta(t)$  being a GWN, the expectation value of their product factorizes. We have

$$\langle E_n \rangle = \exp \left( \frac{1}{2} \kappa^2 \sigma^2 \frac{b_n^2 T}{1 + b_n k_b T} \right) \quad (10)$$

(cf. [8]), and

$$\langle a_{n+1} \rangle = a_0 + \frac{\langle a_n \rangle}{(1 + b_n k_b T)^\mu} \exp \left( \frac{1}{2} \kappa^2 \sigma^2 \frac{b_n^2 T}{1 + b_n k_b T} \right). \quad (11)$$

In the limit  $n \rightarrow \infty$  we replace  $b_n$  by  $b_\infty$  and (11) yields

$$\langle a_\infty \rangle = a_0 \left[ 1 - (1 + b_\infty k_b T)^{-\mu} \exp \left( \frac{1}{2} \kappa^2 \sigma^2 \frac{b_0}{k_b} \right) \right]^{-1}. \quad (12)$$

There is a maximal admissible noise level

$$\kappa^2 \sigma_{\max}^2 = \frac{2k_a}{b_0} \ln(1 + b_\infty k_b T) \quad (13)$$

beyond which the process diverges.

We also need to specify a variance of the process  $a_n$ :

$$\begin{aligned} v_{n+1}^2 &= \langle a_{n+1}^2 \rangle - \langle a_{n+1} \rangle^2 \\ &= \frac{v_n^2 \langle E_n^2 \rangle + \langle a_n \rangle^2 (\langle E_n^2 \rangle - \langle E_n \rangle^2)}{(1 + b_n k_b T)^{2\mu}}. \end{aligned} \quad (14)$$

It is easy to verify that the series  $\{v_n^2\}$  converges for  $\kappa^2 \sigma^2 < \frac{1}{2} \kappa^2 \sigma_{\max}^2$  and diverges for higher noise levels.

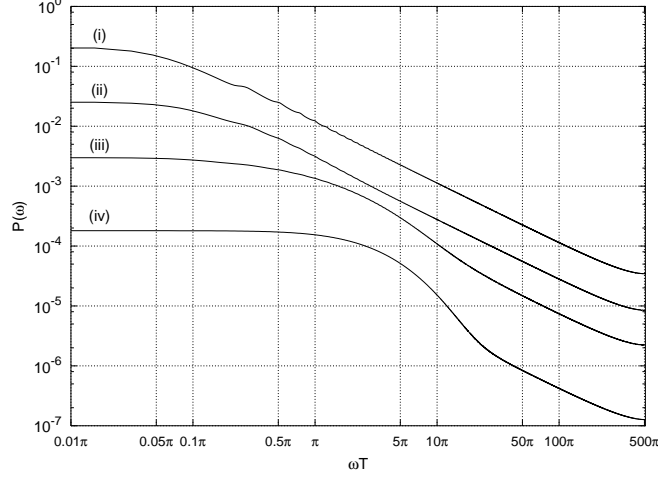


FIG. 1: Power spectra corresponding to the correlation function (19): (i)  $\mu = 1$ ,  $b_0 = 1$ , (ii)  $\mu = 2$ ,  $b_0 = 1$ , (iii)  $\mu = 2$ ,  $b_0 = 10$ , (iv)  $\mu = 5$ ,  $b_0 = 10$ . Other parameters are  $a_0 = 1$ ,  $k_b = 1$ ,  $T = 4$ . In each case  $\kappa^2 \sigma^2 = 0.45 \kappa^2 \sigma_{\max}^2$ . Note a changing slope of the spectrum (iv).

Finally we need to examine the autocorrelation structure of the process  $a(t)$ . We define

$$C(t, \tau) = \langle a(t)a(t + \tau) \rangle - \langle a(t) \rangle \langle a(t + \tau) \rangle . \quad (15)$$

For a GWN we obtain

$$C(nT, mT) = (\langle a_n^2 \rangle - \langle a_n \rangle^2) \prod_{i=0}^{m-1} B_{n+i} \langle E_{n+i} \rangle , \quad (16)$$

where  $B_l = (1 + b_l k_b T)^{-\mu}$ . Note that all  $E_l$ 's in (16) are defined on mutually disjoint intervals and depend on times later than  $nT$ . For  $n \gg 1$ , when the process reaches its stationary state, (16) simplifies to

$$C(nT, mT) \simeq C_m = v_\infty^2 \left( \frac{\exp(b_0 \kappa^2 \sigma^2 / (2k_b))}{(1 + b_\infty k_b T)^\mu} \right)^m \quad (17)$$

provided that  $\kappa^2 \sigma^2 < \frac{1}{2} \kappa^2 \sigma_{\max}^2$ .

The Fourier transform of the autocorrelation function (17) is by the Wiener–Khinchin theorem related to the power spectrum of the process  $\{a_n\}$ ,  $n \gg 1$ , averaged over realizations of the noise:

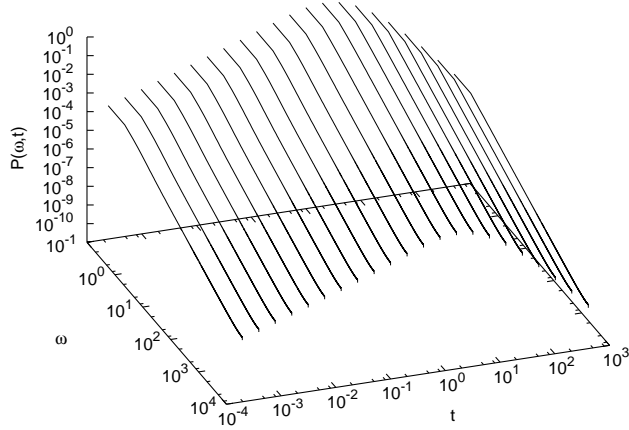


FIG. 2: Time-dependent spectrum of the system not sustained from outside. For all times  $t$ , the power spectrum displays a clear power-law behavior for large  $\omega$ . Parameters are  $\mu = 1$ ,  $b_0 = 1$ ,  $a_0 = 1$ ,  $k_b = 1$ ,  $\kappa^2\sigma^2 = 1.98$ . Units of  $\omega$ ,  $t$  are reciprocal, but otherwise arbitrary.

$$\begin{aligned}
 P(\omega) &= v_\infty^2 \left| \sum_{m=0}^{\infty} \alpha^m e^{im\omega T} \right| \\
 &= \sqrt{2} v_\infty^2 \sqrt{\frac{1 - \alpha \cos \omega T}{1 - 2\alpha \cos \omega T + \alpha^2}},
 \end{aligned} \tag{18}$$

where  $\alpha = (1 + b_\infty k_b T)^{-\mu} \exp(b_0 \kappa^2 \sigma^2 / (2k_b))$ . For all noise levels such that  $v_\infty^2$  is finite the series in (18) is convergent. Because (18) corresponds to the power spectrum of a discrete time series “sampled” with a time step of  $T$ , there is a finite Nyquist frequency  $\pi/T$ . If we want to probe higher frequencies, we need to examine correlations in the process  $a(t)$  *between* the influxes of the reagents. It is sufficient to calculate  $C(nT, \tau)$  with  $\tau = mT + \tau^*$ , where  $m$  is natural and  $0 \leq \tau^* < T$ . For  $n \gg 1$ ,  $C(nT, \tau) \simeq C(\tau)$  with

$$C(\tau) = \frac{C_m}{(1 + b_\infty k_b \tau^*)^\mu} \exp\left(\frac{1}{2} \kappa^2 \sigma^2 \frac{b_\infty^2 \tau^*}{1 + b_\infty k_b \tau^*}\right). \tag{19}$$

The correlation function (19) corresponds to the power spectrum of  $a(t)$  averaged over realizations of the noise. Typical spectra are plotted in Fig. 1. For low frequencies,  $\omega T < \pi$ , which correspond to large  $\tau$ , the spectra are dominated by the behavior similar to (18). For very large frequencies (very small  $\tau$ ), all curves plotted display a clear  $1/f$  (or  $1/\omega$  in our notation) decay. This effect is generic: If we expand (19) in powers of  $\tau^*$ , we get

$$C(\tau) \simeq C_m \left[ 1 - b_\infty (\mu k_b - \frac{1}{2} \kappa^2 \sigma^2 b_\infty) \tau^\star \right] + O((\tau^\star)) . \quad (20)$$

For very small  $\tau^\star$ , the correlation function approaches a non-zero value, which is responsible for the  $1/f$  decay at very large frequencies. The second term in the expansion would lead to  $1/f^2$  decay for intermediate frequencies; however, as  $\tau^\star$  cannot grow too large, this effect can show up only if the coefficient is large enough (cf. spectrum (iv) on Fig. 1). If the time interval,  $T$ , between the consecutive influxes is large,  $\tau^\star$  can also be large and (19) simplifies to

$$C(\tau) \simeq \frac{C_m \exp(\kappa^2 \sigma^2 b_\infty / 2 k_b)}{(1 + b_\infty k_b \tau^\star)^\mu} \sim C_m (1 + b_\infty k_b \tau^\star)^{-\mu} . \quad (21)$$

The coefficient in the above expression can be made sufficiently large by choosing appropriate values of the parameters of the system.

The spectra of Fig. 1 become flat for very high frequencies, but this is a numerical effect resulting from the roundoff errors acting like a white noise.

Let us compare the above results with the situation in which the reactions (1)–(2) are not sustained from outside,  $j_a = j_b = 0$ . Such reactions can be experimentally realized in a closed reactor, as opposed to the flow reactor considered above, but formally this corresponds to taking  $T \gg 1$  and considering the first interval only. Under these assumptions we obtain

$$\langle a(t) \rangle = \mathcal{Z}(t) e^{\Psi(t)}, \quad (22a)$$

$$C(t, \tau) = \mathcal{Z}(t) \mathcal{Z}(t + \tau) \left( e^{4\Psi(t) + \Phi(t, \tau)} - e^{\Psi(t) + \Psi(t + \tau)} \right), \quad (22b)$$

where

$$\begin{aligned} \mathcal{Z}(x) &= \frac{a_0}{(1 + b_0 k_b x)^\mu}, \quad \Psi(x) = \frac{1}{2} \kappa^2 \sigma^2 \frac{b_0^2 x}{1 + b_0 k_b x}, \\ \Phi(x, y) &= \frac{1}{2} \kappa^2 \sigma^2 \frac{b_0^2 y}{(1 + b_0 k_b x)(1 + b_0 k_b (x + y))}. \end{aligned}$$

If  $\tau = 0$ , the second of equations (22) gives the variance of the process  $a(t)$ . We can see that for small  $t$  the variance grows linearly, then reaches a maximum, and then decays;

for long times this decay has a power tail  $\sim t^{-2\mu}$  regardless of the noise level: for times large enough almost all realizations of the process  $a(t)$  vanish, and therefore a statistical difference between these realizations vanishes as well. This is clearly related to the presence and behavior of  $b(t)$ . Recall that a decrease in  $b(t)$  limits the rate at which the substance A decays. For long times, when  $b(t) \simeq 0$ , even wide fluctuations of the reaction rate  $K$  have little effect on the actual decay of A. If the concentration of B were kept constant ( $k_b = 0$ ), the expectation value of  $a(t)$ , its variance and correlations described by (22) would either exponentially go to zero or exponentially diverge, depending on the noise level.

Because in the not sustained case the process  $a(t)$  does not reach any stationary state, the correlation function (22b) depends on two arguments and the corresponding power spectrum,  $P(\omega, t)$ , is also time-dependent. In (22b) we easily recognize the same type of small  $\tau$  behavior as in (19) which leads to the  $1/f$  tail for large frequencies. Indeed, this is what we observe numerically (Fig. 2). Note that this power tail does not change after averaging over the time,  $t$ :

$$\hat{P}(\omega) = \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} P(\omega, t) dt \quad (23)$$

with  $\mathcal{T} \gg 0$  but finite, also displays this type of large frequencies behavior. We may also expect a slope of  $1/f^2$  type for intermediate frequencies and the parameters of the model large enough, but as time,  $t$ , increases, the frequency range corresponding to such a slope decreases, and for large (actually, not even *very* large) values of  $t$  the effect of the second order in  $\tau$  becomes negligible (Fig. 3). For very large values of the parameters and small  $t$ , even the  $1/f^3$  decay appears for intermediate frequencies, but this effect also disappears as time,  $t$ , grows. The presence of the  $1/f^{1+n}$  slope is, therefore, at most a transient effect, which does not survive time averaging (23). In the limit  $t \rightarrow \infty$ , the correlation function (22b) becomes

$$C(t \rightarrow \infty, \tau) \simeq \frac{\text{const}}{(b_0 k_b t)^{2\mu}} (1 + \tau/t)^{-\mu}, \quad (24)$$

which bears a formal similarity to (21), but as the coefficient is very small, the  $\tau$ -dependence becomes practically unobservable. As we have said, this results from the fact that almost all



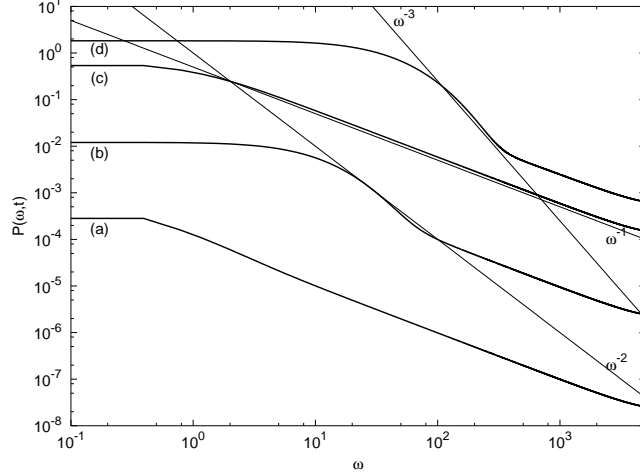


FIG. 3: Time-dependent spectra of the system not sustained from outside. Parameters are: (a)  $\mu = 1$ ,  $b_0 = 1$ ,  $t = 1/2048$ , (b)  $\mu = 5$ ,  $b_0 = 10$ ,  $t = 1/2048$ , (c)  $\mu = 5$ ,  $b_0 = 10$ ,  $t = 1/256$ , (d)  $\mu = 5$ ,  $b_0 = 50$ ,  $t = 1/1024$ . Other parameters, common for all the presented spectra, are:  $a_0 = 1$ ,  $k_b = 1$ ,  $\kappa^2\sigma^2 = 1.98$  (except for (d), where  $\kappa^2\sigma^2 = 0.5$ ). Parameters of the spectra (b), (c) are the same as those of the spectrum (iv) of Fig. 1. Units of  $\omega$ ,  $t$  are reciprocal, but otherwise arbitrary.

realizations of the process  $a(t)$  vanish in the limit  $t \rightarrow \infty$  if the reactions are not sustained from outside.

If the concentration of B is kept constant and the concentration of A is not incremented from outside,

$$C(t, \tau) = a_0 \exp \left( -2b(k_a - b\kappa^2\sigma^2)t - b(k_a - b\kappa^2\sigma^2/2)\tau \right). \quad (25)$$

A similar expression can be found if the concentration of A is incremented from outside. There is no power-law dependence on  $\tau$  in (25). It is now clear that the power-laws in (21) and (24) result from the fact that the stochastic process  $a(t)$  is driven by an “external”, deterministic process  $b(t)$ .

In this Letter we have considered two cases: when the reactions are sustained from outside by periodic influxes of the reagents and when they are not. In the former case, the effects of noise are partially masked by the influxes, but since the noise effects in the latter cannot be observed due to the eventual decay of the reagents (Eqns. (22)), only the former admits a practical experimental realization. The mechanism responsible for the emergence of the  $1/f$  noise in the system under consideration is following: kinetics of a process driven by a

multiplicative GWN (the decay of A) is additionally driven by another, deterministic process (the decay of B). To our knowledge, this is the first model in which a clear *physical* cause of the  $1/f$  noise has been established. As no power scalings or other special features have been assumed, even implicitly, our results suggest that this mechanism can have a more universal character. This idea will be pursued in a future research.

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